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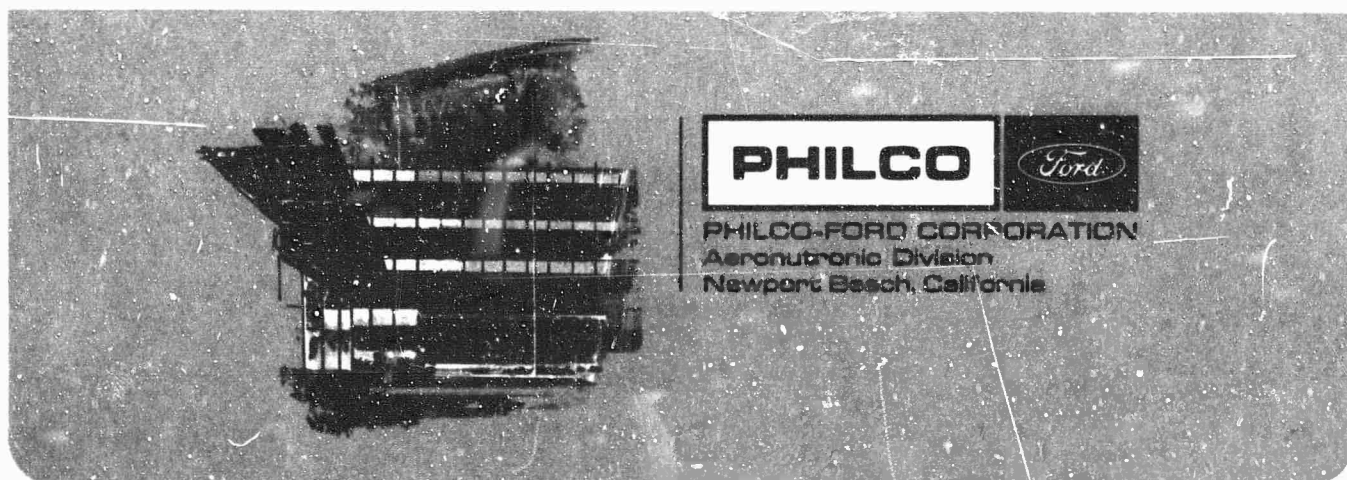
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FINAL TECHNICAL REPORT
THERMODYNAMIC PROPERTIES OF
ROCKET COMBUSTION PRODUCTS

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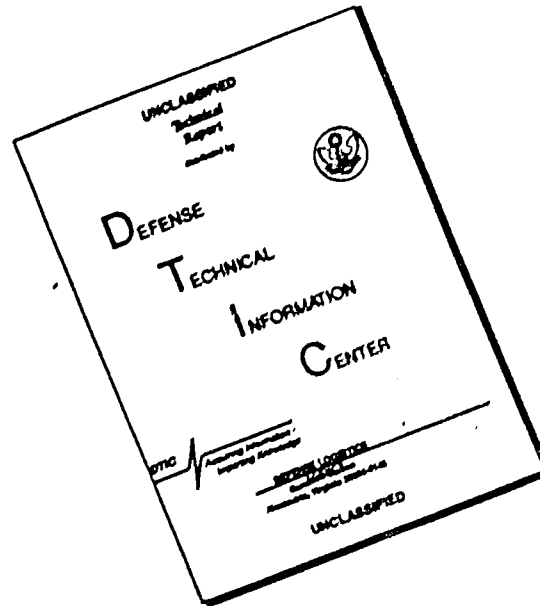


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15 November 1968

FINAL TECHNICAL REPORT

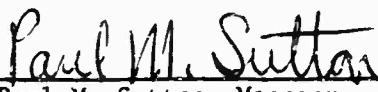
THERMODYNAMIC PROPERTIES OF ROCKET COMBUSTION PRODUCTS

Reporting Period: 15 October 1967 - 15 October 1968

Prepared for: Rocket Propulsion Laboratory
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FOREWORD

This report was prepared by the Aeronutronic Division of the Philco-Ford Corporation under Contract F04611-68-C-0012. The work was administered under the direction of the Rocket Propulsion Laboratory, Air Force Systems Command, with Mr. C. C. Selph as contract monitor.

The authors wish to acknowledge Mr. Robert K. Murray, Supervising Industrial Hygiene Engineer, for coordinating the beryllium safety program and for preparing Section 5 of this report.

The report covers work accomplished during the period 15 October 1967 through 15 October 1968.

This technical report has been reviewed and is approved.

W. H. Ebelke, Colonel, USAF
Chief, Propellant Division

ABSTRACT

This document is the final report on Contract FO4611-68-C-0012. Mass spectrometric studies of various vapor species produced in the H_2 -BeO and in the HCl-BeO systems under Knudsen conditions were carried out at temperatures up to 2485°K. Appropriate equilibrium reactions involving these species were used to determine the heat of formation of BeOH(g). A weighted average of -22.5 kcal/mole is indicated for $\Delta H_{298}^0[\text{BeOH(g)}]$, and the uncertainty is estimated to be ± 6 kcal/mole.

Examination of the mass spectrum for vapor species having the composition $(\text{BeO})_n \cdot \text{H}_2\text{O}$, where $n = 1$ through 5, was conducted. Detectable quantities of such species were not found to be present in the H_2 -BeO system.

Reaction of graphite and beryllium oxide was studied by means of the torsion effusion techniques. Steady-state torsion pressures were not obtainable.

The remaining effort was directed to the redetermination of the fragmentation pattern of the vapor species in the LiF system. A mass spectrometric technique involving beam modulation and phase sensitive detection was used.

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SECTION 1

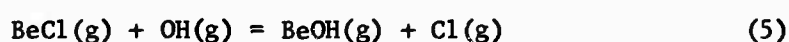
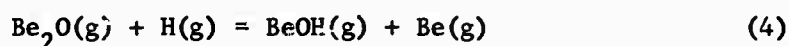
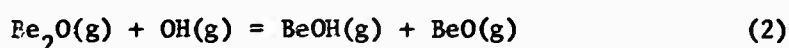
INTRODUCTION AND SUMMARY

Reliable theoretical performance parameters are of considerable utility in the analysis of the actual delivered performance of a propellant system. When measured thrust falls below the calculated value, it may be possible to improve the situation through redesign so as to increase combustion efficiency or minimize heat losses. However, reliable performance data cannot be calculated for many propellant systems of interest because of uncertainties in the thermodynamic properties of key combustion products. This is especially true of beryllium-containing propellant systems.

It is the purpose of this program to provide thermodynamic data for beryllium species in cases where critical uncertainties exist. The principal effort centers on determination of the heats of formation of gaseous species in the Be-O-H system. Other species were studied as the program progressed. The experimental techniques and some of the results obtained are described in the following sections.

Mass spectrometric studies of appropriate species produced in the H_2 -BeO and in the HCl-BeO systems under Knudsen conditions were carried

out at temperatures up to 2485°K using rhenium cell components. Equilibrium constants were evaluated from parent-ions intensities derived from gaseous species involved in the following reactions:



Third law calculations based on these constants gave a weighted average of -22.5 kcal/mole for $\Delta H_f^0_{298} [\text{BeOH(g)}]$, and the uncertainty is estimated to be ± 6 kcal/mole.

As part of this same effort, examination of the mass spectrum for vapor species having composition $(\text{BeO})_n \cdot \text{H}_2\text{O}$, where $n = 1$ through 5, was conducted. Detectable quantities of such species were not found to be present in the H_2 -BeO system at 2425°K; nevertheless, based on an estimate of the minimum perceptible ion current of 2×10^{-13} amps, a limiting heat of $> -263 \pm 16$ kcal/mole was obtained for the heat of formation of $(\text{BeO})_2 \cdot \text{H}_2\text{O(g)}$. Limiting heats are also given for the other hydrated polymeric beryllia species.

Since some question exists as to the final value for the heat of formation of BeO(c), work was directed to a torsion effusion study of the reaction of graphite with beryllium oxide, namely, $\text{BeO(c)} + \text{C(graphite)} = \text{Be(g)} + \text{CO(g)}$. From the heat of this reaction and available thermochemical data, the heat of formation of BeO(c) may be calculated. However, steady state torsion pressures were not achievable.

The remaining effort was given to further development of the mass spectrometric technique involving beam modulation with phase sensitive detection, the purpose of which was to provide a unique method for

identifying the neutral progenitors of a given mass peak. Usually the determination of the molecular progenitors of one or more ion peaks is accomplished by carrying out mass spectrometry under conditions such that only parent ions appear. Some systems (e.g. LiF, LiCl, BeCl₂, etc.), however, do not permit achievement of such conditions, and as a consequence the deduction of vapor composition is compromised.

The major defect in the previous experimental arrangement² as used in the study of the fragmentation pattern of LiF was in the use of an external motor to drive the beam chopper, which required the use of a rotating vacuum seal in the mass spectrometer housing. The O-ring rotary seals were found invariably to leak and produce background in the mass spectrum so high as to make the beam modulation experiment impossible.

After trying various methods, the problem was finally solved; the beam modulation was provided by a chopper wheel driven by a hermetically sealed synchronous motor located inside the mass spectrometer. No pressure rise in the mass spectrometer was detected even after the motor had been operating continuously for several hours.

Beam modulation experiments involving phase sensitive detection were repeated on LiF vapors; phase angle measurements were taken from 1122°K through 1246°K, at approximately 15° intervals. Some anomalies were observed in the results, the most perplexing discrepancy was related to the phase angle for LiF⁺ being smaller than the theoretical angle for LiF. A number of suspected sources for the observed results were postulated and experimentally tested; however, none was found to be entirely satisfactory in unravelling the anomalous behavior of the LiF system.

SECTION 2

THE Be-O-H SYSTEM

2.1 EXPERIMENTAL APPARATUS

The mass spectrometer used in the present study is a Nuclide Analysis Associates Model HT 12-60, a single focusing instrument with a 60° magnetic sector and a 12-inch radius of curvature. It is equipped with a Knudsen cell and an inlet system for the introduction of reactant gas into the cell. A detailed description of this equipment has been given in an earlier report.¹

The Knudsen cell assembly used for the H_2 -BeO and HCl-BeO studies is shown in Figure 1. The cell liner and gas inlet tube were constructed from rhenium metal. Nominal inside dimensions of the cell were 0.75" h x 0.49" dia. The effusion orifice in the rhenium lid was a slit opening whose dimensions were 0.024" wide and 0.104" long. All the joints along the inlet tube were made with press-fitted or ground-fitted unions.

2.2 BEAM MODULATION STUDIES

Earlier experiments² have shown that ion signal levels for several important species in the H_2 -BeO system were extremely low relative to background. It has been reported that significant enhancement in the

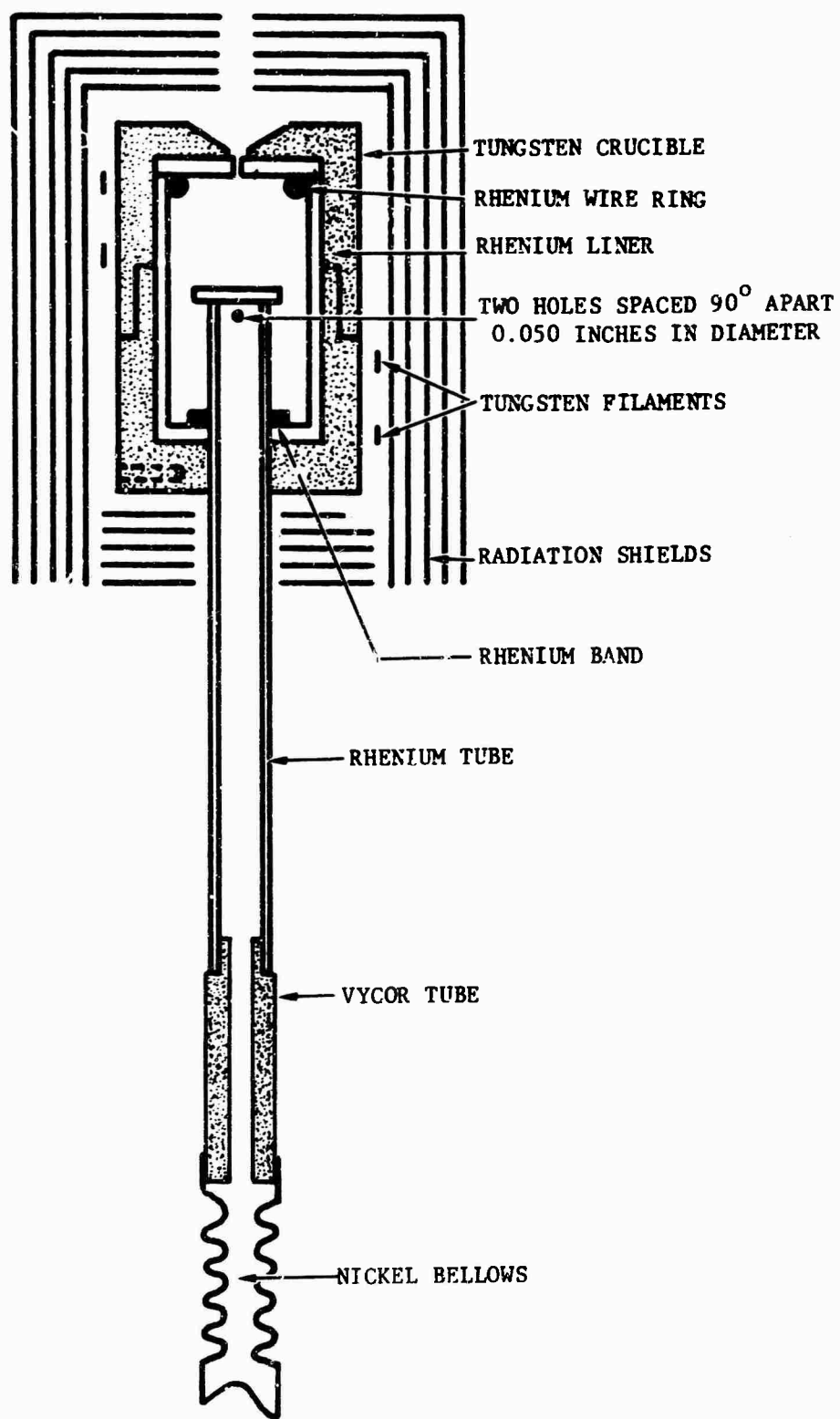


FIGURE 1. KNUDSEN CELL ASSEMBLY

signal to noise ratio can be achieved by modulating the neutral beam at a defined frequency, and subsequently passing the ion signal through a narrow band amplifier tuned to the modulation frequency. Attempts were made to use this procedure in the present studies. The principles of beam modulation and the experimental arrangement have been fully discussed in previous reports.^{2,3,4} Modulation of the molecular beam was carried out with an electrically driven tuning fork chopper mounted on a copper plate which was in turn fastened to the movable shutter located between the Knudsen cell and the ion source. Such an arrangement was necessary so that the shutter could be moved without introducing problems of misalignment between the shutter slit and the openings in the chopper vanes. It was required that the chopper be cooled, particularly when the Knudsen cell temperature exceeded 1400°C. Without cooling its temperature rose above the safe operating point of 150°C. Cooling was provided by passing water through a flexible copper coil soldered to the mounting plate carrying the chopper unit.

The beam modulation system involving the chopper and the tuned amplifier was tested and found to perform satisfactorily, but to provide no improvement in signal to noise ratio. With low level ion signals relative to background, as in the case for BeOH^+ , signal discrimination was indeed found to be somewhat worse than that obtainable by unmodulated techniques. Neither the use of reasonably long time constant for the output RC filtering on the lock-in amplifier nor the filtering of the input signal to this amplifier resulted in significant improvement. For these reasons beam modulation work was abandoned and the study on the H_2 -BeO system was carried out using conventional mass spectrometric techniques.

2.3 STUDIES ON THE H_2 -BeO SYSTEM

The beryllia-containing Knudsen cell was heated initially by thermal radiation from two helically suspended tungsten filaments, keeping the pressure in the mass spectrometer below 10^{-6} torr. The temperature was raised slowly to approximately 1450°K, the temperature limit achievable

by filament heating. Beyond this point, heating was continued by electron bombardment until the desired working temperature was reached. The upper limit attainable was about 2500°K. Temperature was measured with an optical pyrometer which was calibrated against an NBS certified strip lamp.

When a constant working temperature was attained, ionization efficiency curves for Be^+ , O^+ , BeO^+ and Be_2O^+ were determined in the absence of hydrogen flow and those for H^+ , OH^+ and BeOH^+ in the presence of hydrogen flow. The ion intensities were measured both at a given ionizing electron energy and at zero ionizing energy, in each case first with the shutter open and then with the shutter closed. The shutterable intensity at zero electron energy represents the contribution from anomalous ion which must be subtracted from the shutterable ion signal determined at finite electron energy values. The ionization efficiency curves obtained by this procedure were interpreted either by the semi-logarithmic plot method or by the vanishing current method to ascertain the appearance potential of the ion species. Typical curves for OH^+ and BeOH^+ are given in Figure 2; curves for the other more abundant ion species were not illustrated. Background mercury was used as a calibrant gas to fix the electron energy scale. Appearance potentials obtained are given in Table I and are seen to be in good agreement with published data. It is noteworthy that the appearance potential for BeOH^+ is essentially equal to that for BeF^+ (A.P. = 9.1 ev), as predicted by Professor R. F. Porter⁵ based on the fact that alkali hydroxides and fluorides have been found to have approximately the same appearance potentials.

After the appearance potential for a given ion was determined a shutter profile for this ion was taken in the customary way, namely, by moving with a micrometer drive a shutter or shutter slit across the molecular beam and observing the variations in the ion current as a function of shutter position. Low ionizing electron energies were used, usually 4 volts above appearance potential. Appropriate anomalous ion corrections were applied.

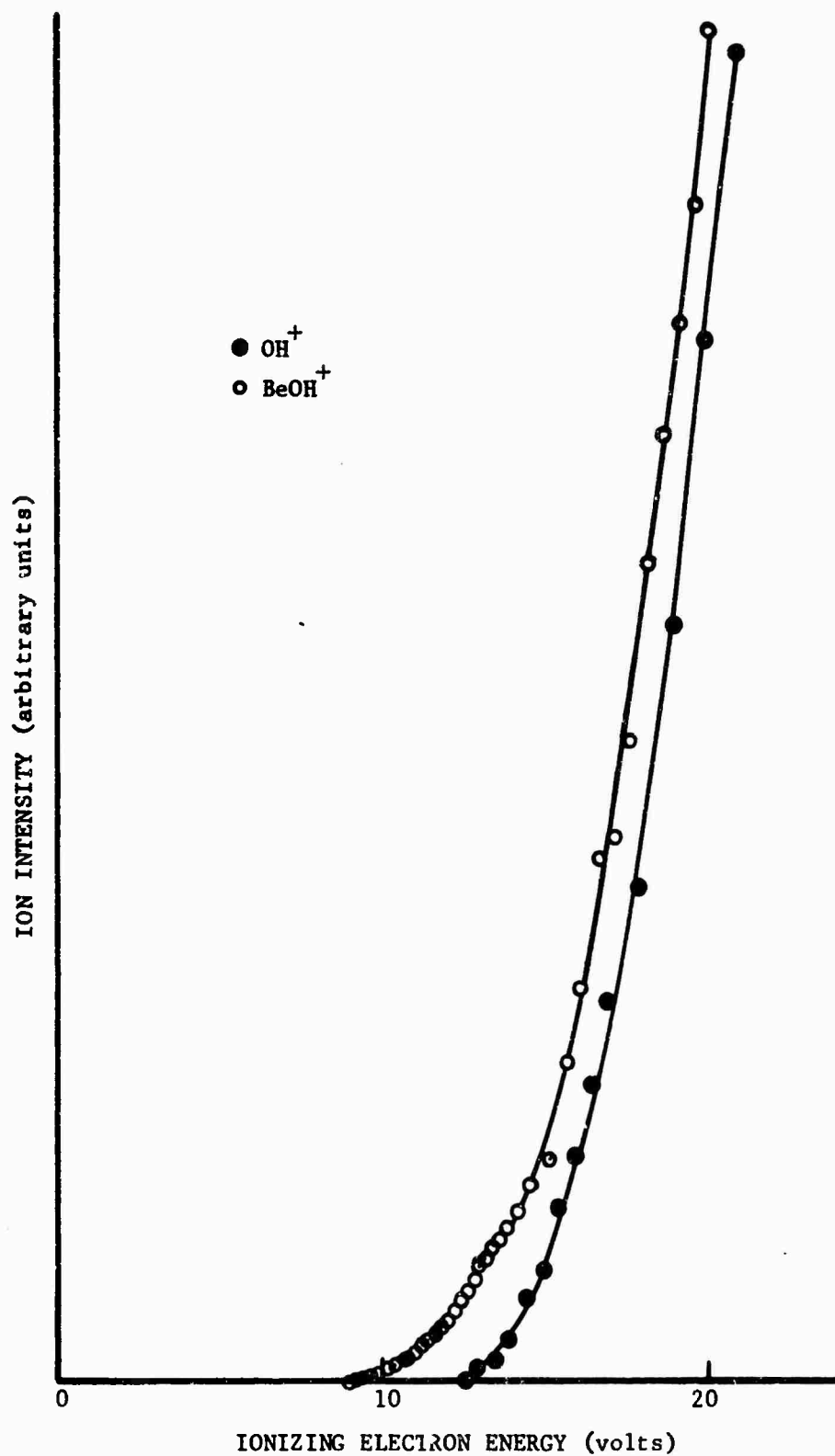


FIGURE 2. IONIZATION EFFICIENCY CURVES FOR OH^+ AND BeOH^+

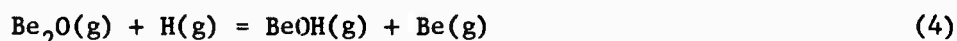
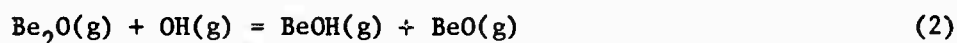
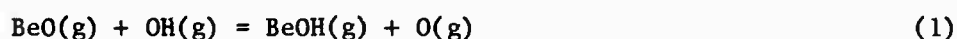
TABLE I. MASS SPECTRAL DATA FOR SPECIES IN H₂-BeO SYSTEM

Ion	A.P., ev		Relative Ionization Cross Section (b)	Relative Multiplier Efficiency	Intensity, arbitrary units (a)			
	Experimental	Literature			2427°K (c)	2422°K	2425°K	2490°K (c)
H ⁺	13.4 ± 0.2	13.6 ⁶	1.00	1.02	0.27	640	1290	615
Be ⁺	9.2 ± 0.2	9.3 ± 0.2 ⁷	6.31	1.15	454	590	610	1830
O ⁺	14.2 ± 0.3	13.6 ⁶	3.29	1.33	166	190	196	575
OH ⁺	12.7 ± 0.5	12.8 ⁶ , 13.2 ⁸	4.29	1.35	0	9.0	13.6	9.0
BeO ⁺	10.1 ± 0.4	10.1 ± 0.4 ⁷	9.60	1.36	8.4	12.7	13.3	43.5
BeOH ⁺	9.0 ± 0.5	--	10.60	1.36	0.06	2.04	3.25	2.65
Be ₂ O ⁺	9.9 ± 0.5	10.5 ± 0.5 ⁹	15.91	1.34	1.8	2.0	2.4	9.99

- (a) Intensities observed with ionizing energies 4 ev above appearance potentials.
- (b) Obtained by adding the relative atomic ionization cross-sections given in reference 10.
- (c) Intensities derived without H₂ flow.

Some typical shutter profiles are given in Figure 3. Curves for Be^+ and O^+ each show a small shoulder on the right side of peak intensity, indicating ions from background gases present inside the can of the radiation shields. Analysis of these curves reveals that the extraneous ions make negligibly small contribution to the peak intensity. Profiles for the other ions are observed to exhibit virtually normal shutter behavior.

From the foregoing observations, the shutter positions at 80 and 0 were selected to define, respectively, the shutter open and shutter closed conditions. Shutterable intensities of parent ions derived from gaseous species involved in the following reactions were then measured. In each case an ionizing electron energy four volts above appearance potential was used, thereby minimizing fragmentation effects.



The measurements were performed at temperatures up to 2490°K under various hydrogen pressures. In each case appropriate anomalous ion corrections were determined and applied in the manner already discussed. The corrected ion intensities are given in Table I along with other mass spectral data. Included are relative ionization cross sections computed from atomic ionization cross section data reported by Otvos and Stevenson.¹⁰ The relative electron multiplier efficiency was determined experimentally by measuring the electron current from the multiplier and the ion beam current from the Faraday cup. The gain is the ratio of these two currents. Multiplier gains were determined for the more intense mass peaks and the values were plotted as a function of mass. The relative electron multiplication efficiencies for the less abundant ions were taken from this graph.

The observed ion intensities listed in Table I were corrected for the relative ionization cross sections and relative multiplier efficiencies,

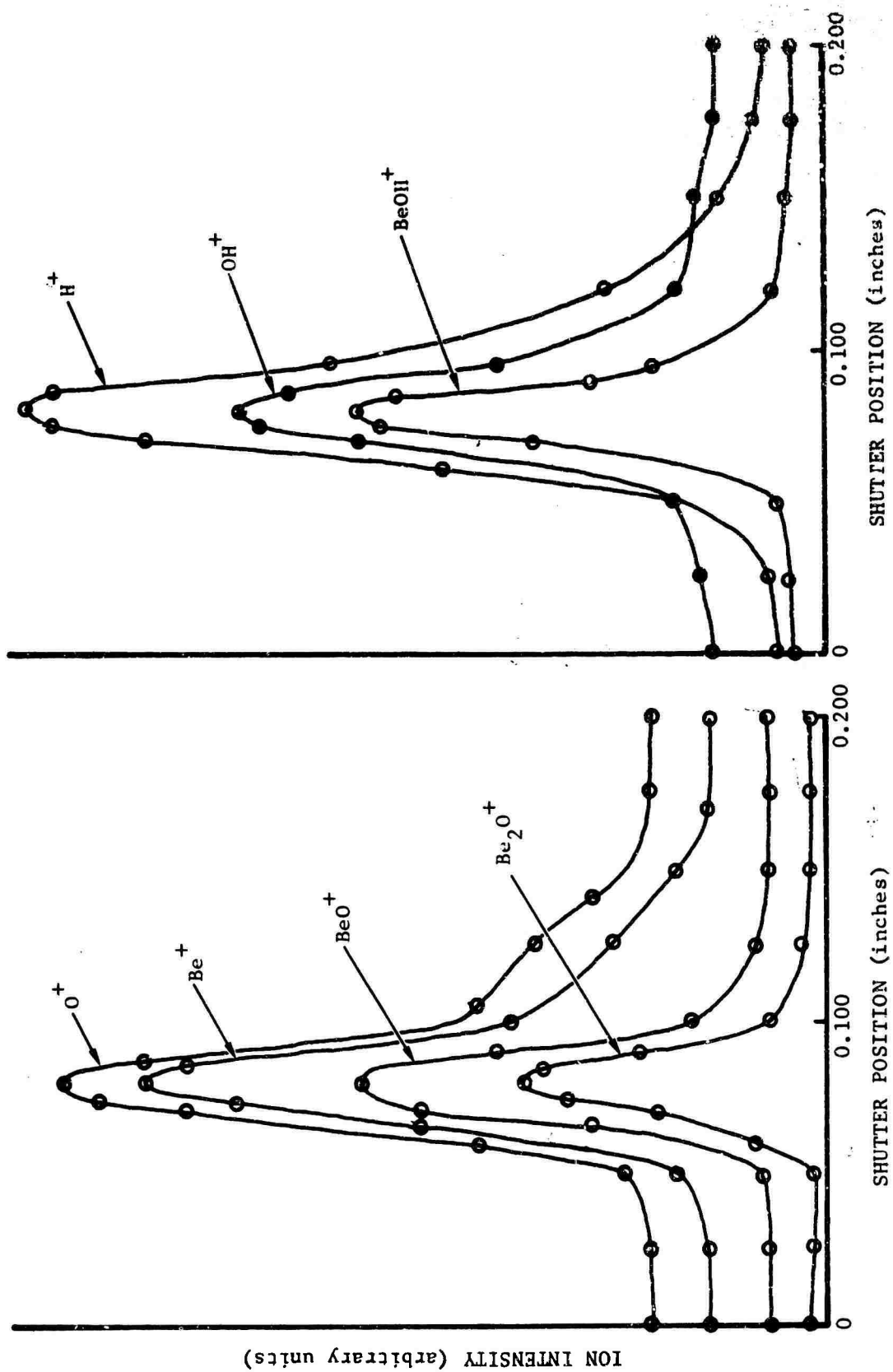


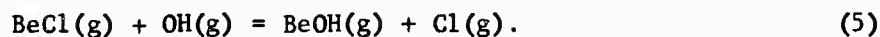
FIGURE 3. SHUTTER PROFILES OF VARIOUS SPECIES IN THE H_2 -BeO SYSTEM

and the equilibrium constants for reactions (1-4) were evaluated from the corrected values. No pressure calibration was required since the equilibrium constants for these reactions are dimensionless.

Results of third law calculations based on these equilibrium constants and on the auxiliary thermodynamic values found in the JANAF Thermochemical Tables¹¹ are given in Table II. The heats of formation for BeOH(g) derived from reactions (1-4) are, respectively, -24.5 ± 8 , -32.5 ± 16 , -10.0 ± 16 , and -25.5 ± 20 kcal/mole. The plus and minus values assigned to each heat were estimated by considering the uncertainties in the published thermochemical data, and the probable errors in the measured intensities, in the temperature and in the computed ionization cross sections. The uncertainties were apportioned as follows: for reactions (1) and (2), 1.5 kcal was assigned to the measured intensities, 1.5 kcal to the ionization cross sections and 0.5 kcal to the temperature, leaving, respectively, 4 and 12 kcal to the thermochemical data for the two reactions. For reactions (3) and (4), approximately the same uncertainties were assigned to the measured intensities and temperatures as before, 8 kcal to the ionization cross sections and, respectively, 4 and 10 kcal to the thermochemical data. The values for the heat of formation of BeOH(g) are seen to differ considerably; nevertheless, they agree within the estimated uncertainties. A weighted average of -23.6 ± 6 kcal/mole is indicated for $\Delta H_{298}^0[\text{BeOH(g)}]$.

2.4 STUDIES ON THE HCl-BeO SYSTEM

To provide additional information in support of the value derived for the heat of formation of BeOH(g) the study was extended to include the HCl-BeO system. In addition to the ions observed in the H₂-BeO study, the ions Cl⁺ and BeCl⁺ were observed, making possible the measurement of the equilibrium constant for reaction (5).



The molecular gaseous species were produced by the addition of a reactant-gas mixture consisting of H₂ and HCl to a Knudsen cell containing

TABLE II. CALCULATIONS FOR REACTIONS INVOLVING BeOH(g)

<u>T°K</u>	<u>K^(a) eq.</u>	<u>ΔH_{298}° (Reaction)</u> <u>(kcal)</u>	<u>ΔH_{298}° [BeOH(g)]</u> <u>(kcal)</u>	<u>H₂ Pressure</u>
$\text{BeO(g)} + \text{OH(g)} = \text{BeOH(g)} + \text{O(g)}$				
2422	4.07	-5.21	-24.4 ± 8	low
2425	4.22	-5.61	-24.8 ± 8	high
2485	4.67	-5.99	-24.2 ± 8	low
			Ave: -24.5 ± 8	
$\text{Be}_2\text{O(g)} + \text{OH(g)} = \text{BeOH(g)} + \text{BeO(g)}$				
2422	1.11	3.84	-32.8 ± 16	low
2425	1.02	4.35	-32.3 ± 16	high
2485	1.00	4.39	-32.3 ± 16	low
			Ave: -32.4 ± 16	
$\text{BeO(c)} + \text{H(g)} = \text{BeOH(g)}$				
2422	2.25×10^{-4}	80.5	-10.5 ± 16	low
2425	1.78×10^{-4}	81.8	-9.2 ± 16	high
2485	3.04×10^{-4}	80.5	-10.5 ± 16	low
			Ave: -10 ± 16	
$\text{Be}_2\text{O(g)} + \text{H(g)} = \text{BeOH(g)} + \text{Be(g)}$				
2422	1.94×10^{-1}	15.0	-26.2 ± 20	low
2425	1.33×10^{-1}	16.5	-24.6 ± 20	high
2485	1.64×10^{-1}	15.6	-25.6 ± 20	low
			Ave: <u>-25.4 ± 20</u>	
			Weighted Ave: -23.6 ± 6	

(a) Derived from ion intensities after correcting for relative ionization cross section and relative electron multiplier efficiency.

beryllia heated to temperatures up to 2518°K. Gas mixtures having H₂ to HCl composition of 25 to 1 and 15 to 1 by volume were used. Attempts to use pure HCl proved unsuccessful; in this case contributions from anomalous ions obscured the shutterable ion intensity of interest.

Shutterable intensities of parent ions derived from gaseous species involved in reaction (5) were measured using ionizing electron energies four volts above their respective appearance potentials. Each of these ions was found to exhibit a normal shutter profile. The electron energy scale was calibrated using background mercury. No appearance potential measurements were made for Cl⁺ and BeCl⁺; instead the published values of 13.0⁶ and 9.5¹² volts were used respectively for these ions. This approach seemed not unreasonable since the appearance potentials determined for the various species in the preceding work were in good agreement with the literature values.

The observed ion intensities were corrected for anomalous ion contributions in the manner already discussed. The corrected ion intensities are given in Table III along with other mass spectral data. Using these values and the relative ionization cross sections and electron multiplier efficiencies given, the equilibrium constants for reaction (5) were evaluated. Results of third law calculations based on these equilibrium constants and on the available heats of formation are shown in Table IV. An average value of -21.3 ± 6.5 is indicated for the heat of formation of BeOH(g). The uncertainty estimated for this heat was apportioned in the following way: 1.5 kcal to the measured intensities, 1 kcal to the ionization cross sections and 4 kcal to the thermochemical data. The heat of formation of BeCl(g) was taken as 14.1 ± 2.2 kcal/mole.¹² All other auxiliary thermochemical data were taken from the JANAF thermochemical Tables.¹¹

2.5 SUMMARY OF RESULTS ON BeOH(g)

It is noteworthy that for the heat of formation of BeOH(g) a value of -21.3 ± 6.5 kcal/mole as derived from reaction (5) and a weighted average of -23.6 ± 6 kcal/mole obtained from reactions (1-4) are found to

TABLE III. MASS SPECTRAL DATA FOR SPECIES IN HCl-BeO SYSTEM

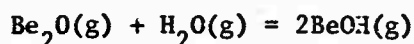
Ion	A.P., ev		Relative Ionization Cross Section (b)	Relative Multiplier Efficiency	Intensity, Arbitrary Units (a)		
	Experimental	Literature			2425°K(c)	2478°K(c)	2518°K(d)
OH ⁺	12.7 ± 0.5	12.8, 13.2	4.29	1.35	7.05	12.6	6.9
BeOH ⁺	9.0 ± 0.5	--	10.60	1.36	1.38	2.0	1.9
Cl ⁺	--	13.0	11.8	1.34	50	96	52
BeCl ⁺	--	9.5	18.11	1.34	1.62	1.90	1.90

- (a) Intensities observed with ionizing energies 4 ev above appearance potentials.
- (b) Obtained by adding the relative atomic ionization cross-sections given in reference 10.
- (c) Reactant gas having H₂ to HCl composition of 25 to 1 by volume was used.
- (d) Reactant gas having H₂ to HCl composition of 15 to 1 by volume was used.

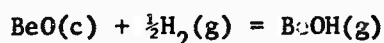
TABLE IV. THIRD-LAW CALCULATIONS FOR A REACTION INVOLVING BeOH(g)

$T^{\circ}\text{K}$	$K_{\text{eq.}}$	$\Delta H_{298}^{\circ}(\text{Reaction})$ (kcal)	$\Delta H_{298}^{\circ}[\text{BeOH(g)}]$ (kcal)
2425	3.73	-14.8	-20.3 \pm 6.5
2478	4.95	-16.5	-22.0 \pm 6.5
2518	4.65	-16.4	-21.9 \pm 6.5
Average:			-21.3 \pm 6.5

be in good agreement with the limiting value of -25 ± 10 kcal/mole obtained by Hildenbrand, Theard and Ju¹³ in their mass spectrometric study of the equilibrium,

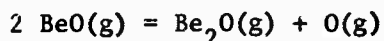


but are not in accord with -48.2 ± 3 kcal/mole as determined by Ko, Greenbaum and Farber.¹⁴ These investigators studied the reaction



using a molecular flow effusion method.

As a supplement to the foregoing summary which is based in part upon data for Be₂O in the JANAF tables, the data presented in Table I, obtained with and without hydrogen flow, permit the evaluation of the heat of formation of Be₂O(g) from the reaction



An average value of -8.3 kcal/mole is obtained as compared to -15 kcal/mole given in the JANAF Thermochemical Tables.¹¹ The estimated uncertainty is ± 10 kcal/mole. Using $\Delta H_{298}^{\circ}[\text{Be}_2\text{O(g)}] = -8.3$ kcal/mole, the heat of formation for BeOH(g) was evaluated for reactions (2) and (4) and found to be, respectively, -25.8 ± 16 and -18.8 ± 20 kcal/mole.

2.6 IDENTIFICATION OF ION SPECIES AT m/e 43

Previous studies² on the H_2 -BeO system gave a highly suspected heat of formation for $Be(OH)_2(g)$, approximately 40 kcal/mole more negative than the published value of -158.5.¹¹ A plausible explanation offered at that time was that the ion species observed at m/e 43 was not $Be(OH)_2^+$. In order to resolve this question the following experiments were conducted.

Shutter profiles at m/e 43 were determined from three separate experiments, one with an empty cell and two with a cell containing BeO. Between each experiment the cell was removed from the mass spectrometer for one reason or another (to unplug the gas inlet tube, to empty or to reload the cell). All intensity measurements were taken 4 volts above the appearance potential for the ion observed at m/e 43. The same H_2 pressure was maintained in all experiments by adjusting the variable leak until the m/e 1 (H^+) peak attained a preselected value. The results of this series of studies are presented in Figure 4.

Curves 1 and 2 were obtained from preliminary experiments in which the cell (filled with H_2 in the first case and empty in the second case) and the shields were outgassed at 2425°K for only a short time prior to taking of the data. The curves show the same general shape. They are broad and their positions of maximum intensity are shifted relative to the Be^+ curve. These observations suggest that the ions are derived from neutral species originating not from the cell but from within the radiation shields and therefore cannot be $Be(OH)_2^+$.

That the ion observed at m/e 43 is not $Be(OH)_2^+$ is afforded conclusive evidence from the third and final experiment. In this case the cell (loaded with BeO) and the shields were outgassed at 2425°K for approximately 40 hours before hydrogen was introduced and measurements were taken. Curve 3 so obtained is flat, showing no shutterable intensity. This behavior demonstrates (1) that a measurable quantity of $Be(OH)_2^+$ is not present in the H_2 -BeO system and (2) that prolonged heating removed the contaminants which, upon reaction with hydrogen, gave rise to the ion intensity

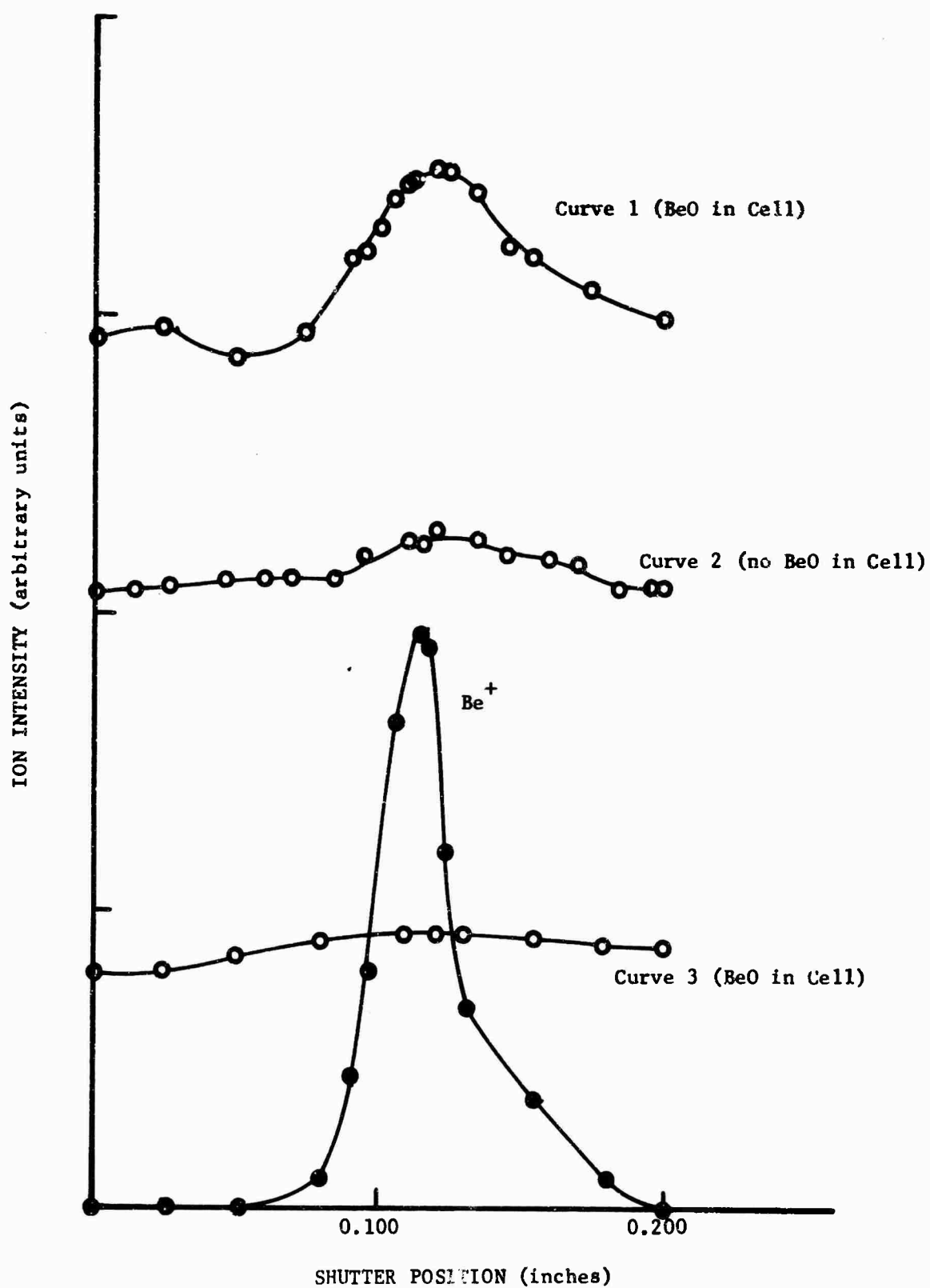


FIGURE 4. SHUTTER PROFILES FOR Be⁺ AND m/e 43 ION SPECIES
 ELECTRON ENERGY: 4 volts above threshold
 TEMPERATURE: ~ 2423°K

originally observed at m/e 43. In view of these results further work on the determination of the heat of formation of $\text{Be}(\text{OH})_2(\text{g})$ seems futile for the present.

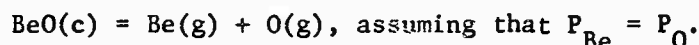
2.7 SEARCH FOR $(\text{BeO})_2 \cdot \text{H}_2\text{O}$, ETC.

In order to search for the postulated polymeric hydrated beryllia vapors,¹³ a scan of the mass spectrum up to mass number 150 was conducted with hydrogen passing into the Knudsen cell which contained BeO , first with the shutter open and then with the shutter closed. The temperature was maintained at $2425 \pm 3^\circ\text{K}$, the hydrogen pressure was comparable to the "low" pressures used in the BeCl_2 studies,* and the ionizing electron energy was 20 e.v. These are the most forcing conditions which we could maintain reliably for the time necessary for the two scans. At significantly higher temperature, the cell supports tend to sag, causing misalignment of the cell with the shutter slit and ion source entrance slits. At higher oxygen potentials, e.g., if water vapor or water vapor-hydrogen mixtures were passed into the cell in place of hydrogen, there are serious problems with anomalous ions, as was also the case when HCl was used as the reactant gas (see paragraph 2.4). Furthermore, it has been observed that when water is used as the reactive gas, only short operating periods are possible due to the degradation of the heating filaments, electrical breakdown and structural failure.¹³

*The hydrogen atom pressure in the cell can be estimated from the expression

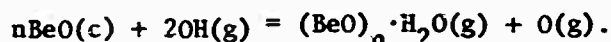
$$P_{\text{H}} = \frac{I_{\text{H}}}{\sigma_{\text{H}}} \frac{\sigma_{\text{O}}}{I_{\text{O}}} P_{\text{O}}.$$

The oxygen pressure was calculated from the temperature and the equilibrium constant for the reaction



The relative ionization cross sections for hydrogen and oxygen, σ_{H} and σ_{O} , and the ion currents for hydrogen and oxygen, were taken from Reference 10 and Table I. The hydrogen pressure was estimated to be 8×10^{-5} atm under these conditions.

From the information obtained in these scans, we may calculate limits for the heats of formation of the BeO polymer hydrates. Most conveniently, this is done by considering the equilibria:



For these approximate computations, we will assume that 20 ev is approximately 4 ev above threshold for the ions of the hydrate vapor species. If the equivalence of the appearance potentials⁵ holds for $\text{Be(OH)}_2^+ - \text{BeF}_2^+$, as it appears to hold for $\text{BeOH}^+ - \text{BeF}^+$, we are not seriously in error here, since AP. $(\text{BeF}_2^+/\text{BeF}_2) = 14.7$ ev. We are thus only 5.3 ev above the appearance potential, an inconsequential error for these estimates. There is no way to estimate the appearance potential for the remaining postulated hydrates.

For OH(g) , O(g) , and BeO(c) the free energy functions were taken from the JANAF Tables. The free energy function for $\text{Be}_2\text{O}_3\text{H}_2(\text{g})$ was estimated as follows: It was assumed that the difference in free energy functions for $\text{Be(OH)}_2(\text{g})$ and $\text{BeF}_2(\text{g})$ is equal to the difference in free energy functions for $\text{Be}_2\text{O}_3\text{H}_2(\text{g})$ and $\text{Be}_2\text{OF}_2(\text{g})$, since these latter two species presumably have similar structures. Thermal functions for Be_2OF_2 are taken from the JANAF Tables. For the free energy functions for the heavier homologs in the series, it was assumed that for each added Be-O unit, a fixed increment equal to the difference between the free energy functions for $\text{Be}_2\text{O}_3\text{H}_2(\text{g})$ and $\text{BeO}_2\text{H}_2(\text{g})$ should be added.

The equilibrium constant for the above reaction is given by

$$K = \frac{(P_{\text{hydrate}})^P P_{\text{O}}}{(P_{\text{OH}})^2} \approx \frac{I_{\text{hydrate}} I_{\text{O}}^{\sigma_{\text{OH}}^2}}{I_{\text{OH}}^2 \sigma_{\text{O}} \sigma_{\text{hydrate}}}$$

Relative cross sections, σ_x , were again summations of the atomic cross-sections taken from Reference 10. The ion current data for O^+ and OH^+ were taken from Table I, column 7, i.e., for the conditions 4 ev over threshold, $T = 2425^\circ\text{K}$ and "low" pressure of hydrogen. The minimum perceptible ion current was estimated to be 2×10^{-13} amps for each of the

hydrate species since there were no disturbing background at these mass numbers, except as has been described above for $m/e = 43$. The estimated limiting heats are given in Table IVA along with other pertinent estimated data. The stated uncertainties are based on reasonable estimates of the possible experimental errors and the uncertainties in the thermal data. A generous uncertainty has been included to account for possible errors in the estimated free energy function of the hydrates. It is encouraging that the estimated limiting heat of formation for $\text{Be}(\text{OH})_2(\text{g}) > -156.3 \pm 9$, kcal/mole agrees with the accepted heat of formation of $\text{Be}(\text{OH})_2(\text{g})$, -156.4 kcal/mole.¹¹ Estimates of the heats of formation of these gaseous hydrates based on bond energy schemes lead us to believe that these reported estimated limiting heats of formation are not unreasonable.

TABLE IVA
THERMOCHEMICAL ESTIMATES FOR THE Be-O-H VAPOR SYSTEM

Species	σ_x	¹ Arbitrary Units	K	$-\Delta(F-H_{298})$ T e. u.	$\Delta H_{298,R}$ Kcal/mole	$\Delta H_{f,298}$ Kcal/mole
$\text{Be}(\text{OH})_2(\text{g})$	14.89	<0.02	$<5.0 \times 10^{-3}$	79.77	$>44.6 \pm 6$	$>-156.3 \pm 9$
$\text{Be}_2\text{O}_3\text{H}_2(\text{g})$	24.5	<0.02	$<3.1 \times 10^{-3}$	109.50	$>81.1 \pm 9$	$>-263 \pm 14$
$\text{Be}_3\text{O}_4\text{H}_2(\text{g})$	34.1	<0.02	$<2.2 \times 10^{-3}$	139.23	$>117 \pm 12$	$>-370 \pm 21$
$\text{Be}_4\text{O}_5\text{H}_2(\text{g})$	43.7	<0.02	$<1.7 \times 10^{-3}$	168.96	$>152 \pm 15$	$>-478 \pm 27$
$\text{Be}_5\text{O}_6\text{H}_2(\text{g})$	53.3	<0.02	$<1.4 \times 10^{-3}$	198.69	$>188 \pm 20$	$>-584 \pm 35$

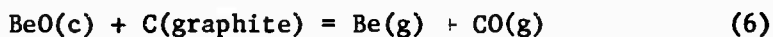
¹ Estimated minimum ion current observable with no serious background interference.

SECTION 3

TORSION-EFFUSION STUDY OF THE REACTION OF GRAPHITE AND BERYLLIUM OXIDE

In the vaporization of BeO the total vapor pressure as derived from torsion-effusion measurements has been found to be higher than that inferred from mass spectrometric experiments. The explanation offered for the discrepancy was that either the accepted value for the heat of formation of crystalline BeO is too negative by ca. 3 kcal/mole or the vapor over crystalline BeO is richer in molecular species (as contrasted to atomic species) than has hitherto been suspected.

To differentiate between these possibilities, the torsion-effusion study, previously initiated,² which aims at providing the heat for the reaction



was continued. From this heat and available thermochemical data, the heat of formation of BeO may be calculated. Since X-ray diffraction analysis of cell residues revealed that no unsuspected Be-O, Be-C or Be-O-C phases were formed, reaction (6) was taken as the equilibrium reaction.

Earlier efforts in the measurement of the pressure generated by reaction (6) at temperatures up to 1900°K were unsuccessful; a steady

torsion pressure was not obtainable. It was speculated that this behavior was due to diminution in the contact area between graphite and beryllium oxide particles as the reaction progressed. Attempts were therefore made to resolve this problem by proper sample preparation and by judicious selection of the orifices in the Knudsen cell so as to minimize sample loss during the experimental run. In the present work pressed BeO-C samples rather than loosely mixed powders were used. Equimolar and two-to-one mole ratio C to BeO powder mixtures were pelletized under a pressure of 17,000 pounds/inch².

Torsion-effusion measurements were carried out on these samples using graphite cells. First, a cell having four 1-mm diameter orifices ($\Sigma afq = 0.01264 \text{ cm}^3$) was used. The cell was heated slowly over a period of several hours to the reaction temperature range and then briefly to 15° above the highest experimental temperature of interest to ensure desorption of adsorbed gases. Observations were taken at 5-10 minute intervals over a period of one hour at each of the following temperatures, held constant at 1867°, 1851° and 1825°K. The pressure was observed to decrease with time.

In the second experiment, in order to reduce the loss of sample from the cell, and thereby minimize the change in contact area, a cell with four 0.6-mm diameter orifices ($\Sigma afq = 0.003235 \text{ cm}^3$) was used. At this time the sensitivity of the torsion fiber was increased approximately 6.1 times to compensate for the smaller angular deflection expected from the use of smaller orifices. Even under such conditions, steady-state torsion pressures were not achievable. Thus, the results to date indicate that unless a simple method is available by which the reaction sites can be replenished as they disappear, there is little hope that study of reaction (6) will yield a reliable value for the heat of formation of BeO(c).

SECTION 4

BEAM MODULATION MASS SPECTROMETRY

This section describes work which is a continuation from the previous contract. Its primary purpose was to demonstrate the soundness of the beam modulation technique involving phase sensitive detection and ultimately its use to provide definitive fragmentation patterns for LiF , LiCl , and BeCl_2 vapors. In order to do this it was necessary to correct a major defect in the previous experimental arrangement, namely, the use of an external motor for driving the beam chopper, which required a rotating vacuum seal in the mass spectrometer housing. Such seals were found invariably to leak and produce backgrounds in the mass spectrum so high as to make the beam modulation experiment impossible.

4.1 MODIFICATIONS OF BEAM MODULATION APPARATUS

In preparation for reinvestigating the fragmentation pattern of LiF vapor, some effort was given in attempts to improve the performance of the beam modulation apparatus. It will be recalled from our previous report² that large variations in the mass spectrometric data for LiF^+ and Li_3F_2^+ were related to the existence of high unsteady background at mass positions where LiF^+ and Li_3F_2^+ ion currents were observed. Available evidence indicated that the source of this high background was the O-rings in the rotary seal.

As a logical step to remove the problem, the O-ring rotary seal was replaced with a bellows-coupled rotary motion feed-through made by Allen-Jones Electronics Corporation. Several attempts to operate with this device were made and each time the pressure in the mass spectrometer increased more than two orders of magnitude. Concomitant with the pressure rise the ion intensity of the mass 26 peak increased approximately 30 times. Previous experiments have shown that even a five fold increase in background intensity is not acceptable. The rotary motion feed-through was returned to the factory and the manufacturer's engineers found several breaks in the bellows seal. The unit was not reparable and a replacement was not available.

In order to avoid the difficulties associated with rotating vacuum seals, the use of a tuning fork chopper previously obtained from the Bulova Watch Company to provide beam modulation was considered. The operational characteristics of this it were determined by causing it to chop a light beam and observing the time-intensity relation for the light passing through the vanes with a photoconductive detector, the output of which was displayed on an oscilloscope. It was found that for the particular tuning fork under study, the dark times of alternate cycles were different, indicating that the inward and outward travels of the vanes were of different periods. Visual observation of the vanes under a strobe light confirmed this unsymmetrical behavior. We have been assured by the manufacturer that this characteristic is very unusual. This unit was returned to the manufacturer for corrective service. Although no delivery date was promised, accounts of past deliveries would indicate that 2-3 months delay was not unexpected. As it was learned later, delivery was not made until two weeks before the end of this contract period.

In the meantime, it was conceived that an a.c. hysteresis synchronous motor could be successfully operated inside the mass spectrometer if the stator were hermetically sealed. Such a motor was developed and the experimental procedures previously described were modified to accommodate its use. The work described in the following was carried out using the new procedures.

4.2 EXPERIMENTAL

The apparatus and method described previously^{2,3} were used with a few modifications. A Knudsen cell placed in the mass spectrometer was heated by thermal radiation from two helically suspended tungsten filaments. The temperature was measured with a Pt/Pt, 13% Rh thermocouple, the bead of which was pressed into a hole drilled into the bottom of a tungsten crucible holding the cell. Graphite cell liners equipped with a lid having a conical effusion orifice 0.025 inches in diameter were used. In some experiments the tungsten crucible itself or a beryllia liner was fitted with a stainless steel lid and used as a Knudsen cell.

Modulation of the molecular beam was carried out in this work with a rotating sector wheel 3.00 inches in diameter and 0.100 inches thick having 24 slots, 0.158 inches wide (at the periphery) and 0.475 inches long. Mechanical assembly considerations required that each slot be cut along the radius line. The wheel was actually comprised of two stainless steel disks, each being 0.050 inches thick and having 24 equally spaced open and closed sectors. Such a design permitted an adjustable aperture, accomplished merely by rotating one disk relative to the other. The disks were adjacently held together by two set screws placed diametrically opposite the center point of the wheel.

The sector wheel so designed was attached directly to a water-cooled, 3600 rpm hysteresis synchronous motor located inside the mass spectrometer. The stator of this motor (manufactured by Globe Industries, Incorporated) was hermetically sealed in an enclosure so that the vacuum sees only the bearings and the solid iron rotor. The bearings were coated, according to the manufacturer, with a dry lubricant having extremely low vapor pressure. Outgassing from these parts was found to be negligible; no pressure rise in the mass spectrometer was detected even after the motor had been operating continuously for several hours.

For some later experiments a second chopper wheel was constructed in which a single aluminum disk 0.050 inches thick was used; all other dimensions were unchanged. The significant modification incorporated was that the trailing and leading edges of each closed sector were provided with sharp edges beveled at 30° .

The lock-in amplifier (Princeton Applied Research, Model JB-5) was tuned by passing the chopped light signal at 1440 Hz into the reference channel and adjusting the frequency control dial to give a maximum output signal. At the same time the phase shifter was set arbitrarily to give a minimum phase difference between the input and output signals; this minimum phase difference was found to be zero degrees. The value itself has no particular significance; the important fact is that this angle remained constant during an experimental run. Repeat observations revealed that this angle did not change more than 0.5° .

The LiF sample used in the present study was pre-treated with HF gas. Lithium fluoride powder (J. T. Baker "Analyzed" Reagent) held in a platinum crucible was heated above its melting point under atmospheric conditions for 15 minutes. The resulting grayish crystals were transferred to a platinum boat which was placed in a nickel tube and slowly heated, during which HF was passed into the tube. The temperature was raised and held above the melting point of LiF for approximately 5 hours. Flow of HF was terminated and argon was passed over molten LiF for 3 hours, then the temperature was slowly lowered to room temperature. The crystals so treated were absolutely clear and colorless.

Dry LiCl crystals were prepared by treating LiCl powder (J. T. Baker "Analyzed" Reagent) with Cl_2 gas. The powder placed in an alumina boat was slowly heated in a stream of Cl_2 . Much of the water was removed at this point. The remaining steps in this procedure were similar to those followed in the preparation of LiF samples. The LiCl crystals were stored in a desiccator over MgClO_4 and handled only in a dry-box.

4.3 STUDIES ON THE LiF SYSTEM

In initial experiments the LiF vapor was produced by heating LiF crystals in a graphite Knudsen cell. Phase angle measurements were taken, as previously discussed,² by adjusting the dial on a phase generator so that the trace of the lock-in amplifier output on a strip chart recorder remained on the zero signal line. The phase angles given by the dial setting were corrected for the instrumental phase shift. The correction was derived from the Li_3F_2^+ species based on the assumption that its only progenitor is Li_3F_3 . The angles so corrected are summarized in Table VI.

The phase positions of the pure precursors were determined from theoretical curves computed for three temperatures. Linear interpolation was used to obtain the theoretical phase angles at other temperatures. In these computations the computer program was modified to derive the shutter functions from a table of values of percent of full open position versus time, initially inserted into the problem. The table used in this work is given as Table V. It represents a trapezoidal form, obtained by cutting off a triangle at a specified point below the apex. A test of the conformity between the theoretical curve for Li_3F_3 and the experimental points for Li_3F_2^+ is shown in Figure 6; similar comparison is made in Figure 7 for Ag and Ag^+ data acquired from later work. In preparing these figures, the instrument phase shift was adjusted to give the best fit between the points and the curves. The general conformity between experimental and theoretical curves is excellent.

The experimental phase angles presented in Table VI are found to show a slight temperature dependency, tending toward larger values at high temperatures whereas the velocity distribution theory predicts a trend toward smaller values for the precursors. This trend is clearly illustrated in Figure 5 by a plot of the difference between the measured phase angles and the values for the most obvious neutral precursor. Larger differences are observed as the temperature increases. This is

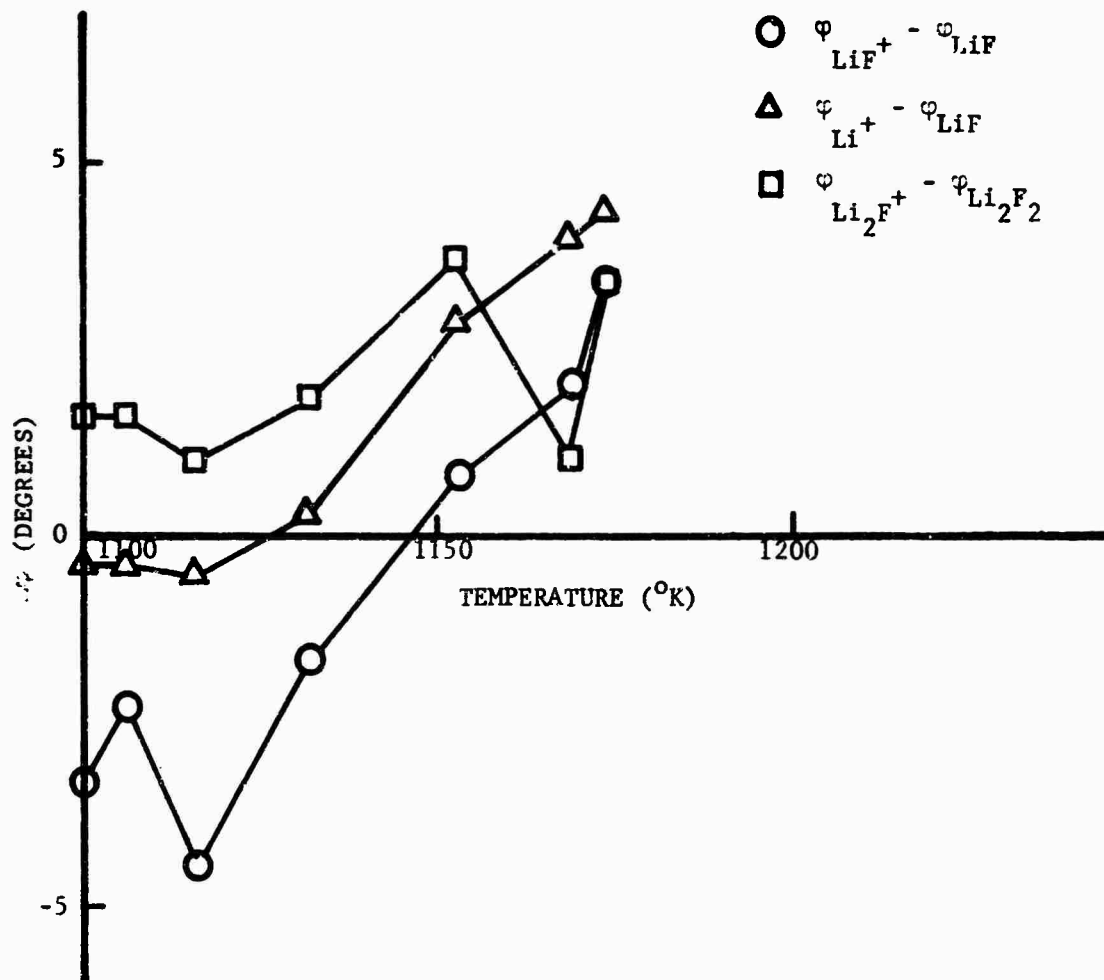


FIGURE 5. PLOT OF DIFFERENCE BETWEEN THE MEASURED PHASE ANGLES AND THE THEORETICAL PHASE ANGLES FOR THE MOST OBVIOUS PRECURSOR (REFERENCE: $\text{Li}_3\text{F}_2^+ - \text{Li}_3\text{F}_3$) VERSUS TEMPERATURE

TABLE V
SHUTTER FUNCTION

<u>Time (ms)</u>	<u>Area (percent open)</u>
0	0
0.0088	20
0.0176	40
0.0264	60
0.0352	80
0.0440	100
0.2350	100
0.2438	80
0.2536	60
0.2614	40
0.2702	20
0.2790	0
0.2810	0

TABLE VI. EXPERIMENTAL AND THEORETICAL PHASE ANGLES OF LiF SYSTEM

Precursor (Theoretical)	Ion (Experimental)	φ							
		1100°K	1106°K	1116°K	1132°K	1153°K	1169°K	1174°K	
LiF	Li ⁺	138.2	138	137.8	137.3	136.6	136	135.9	
		137.9	137.7	137.3	137.6	139.5	140	140.3	
	LiF ⁺	134.9	135.7	133.3	136.6	137.4	138	139.3	
Li ₂ F ₂	Li ₂ F ⁺	161.3	161.1	160.8	160.3	159.6	159	158.9	
		162.9	162.7	161.8	162.1	163.3	160	162.3	
	Li ₃ F ₃	177.9	177.7	177.3	176.6	175.8	175	174.8	
Li ₃ F ₂	Li ₃ F ₂ ⁺	177.9	177.7	177.3	176.6	175.8	175	174.8	

Ionizing electron energy = 70 e.v.

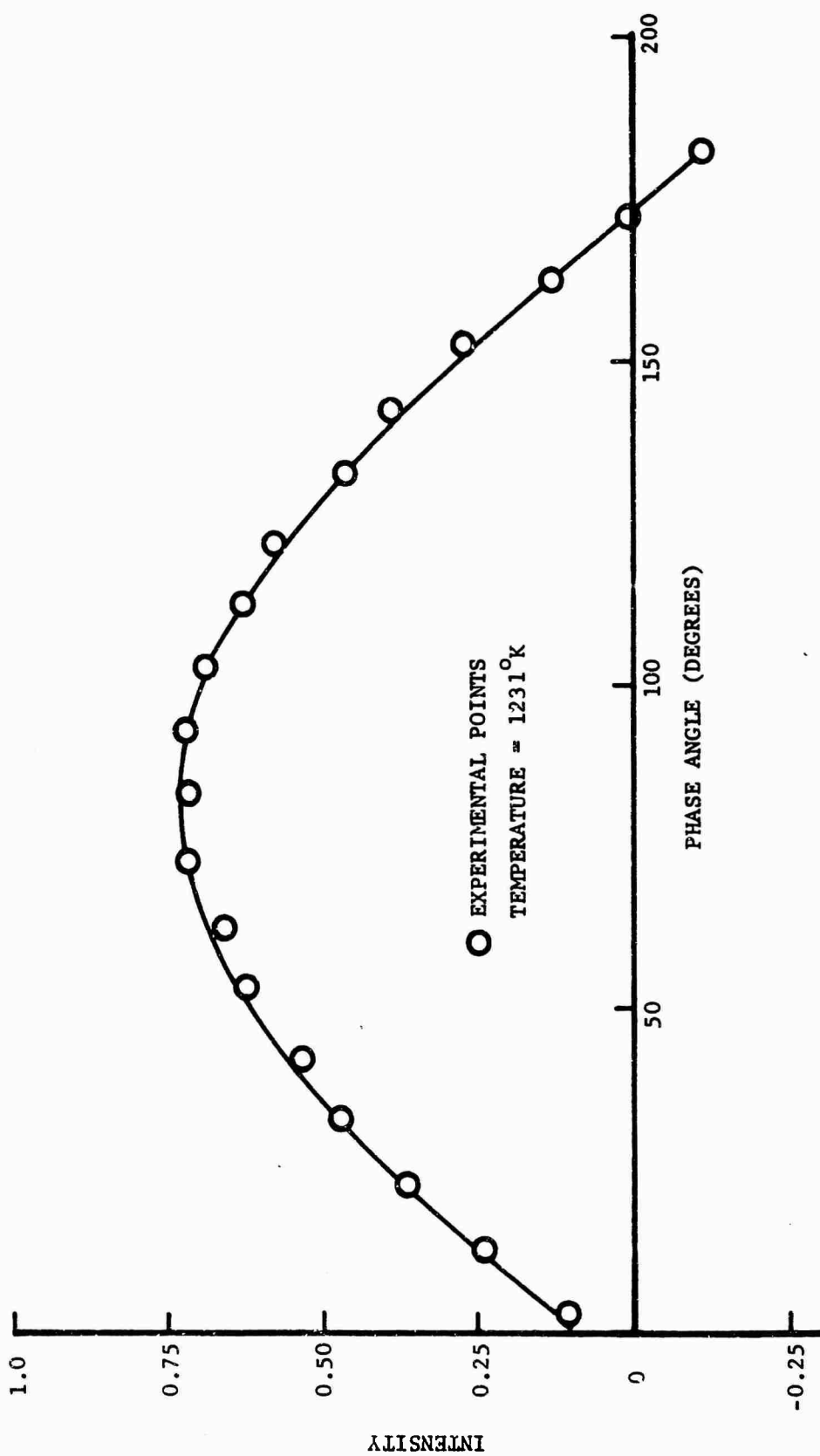


FIGURE 6. COMPARISON OF EXPERIMENTAL POINTS WITH THEORETICAL CURVE FOR $L1.3F_3$

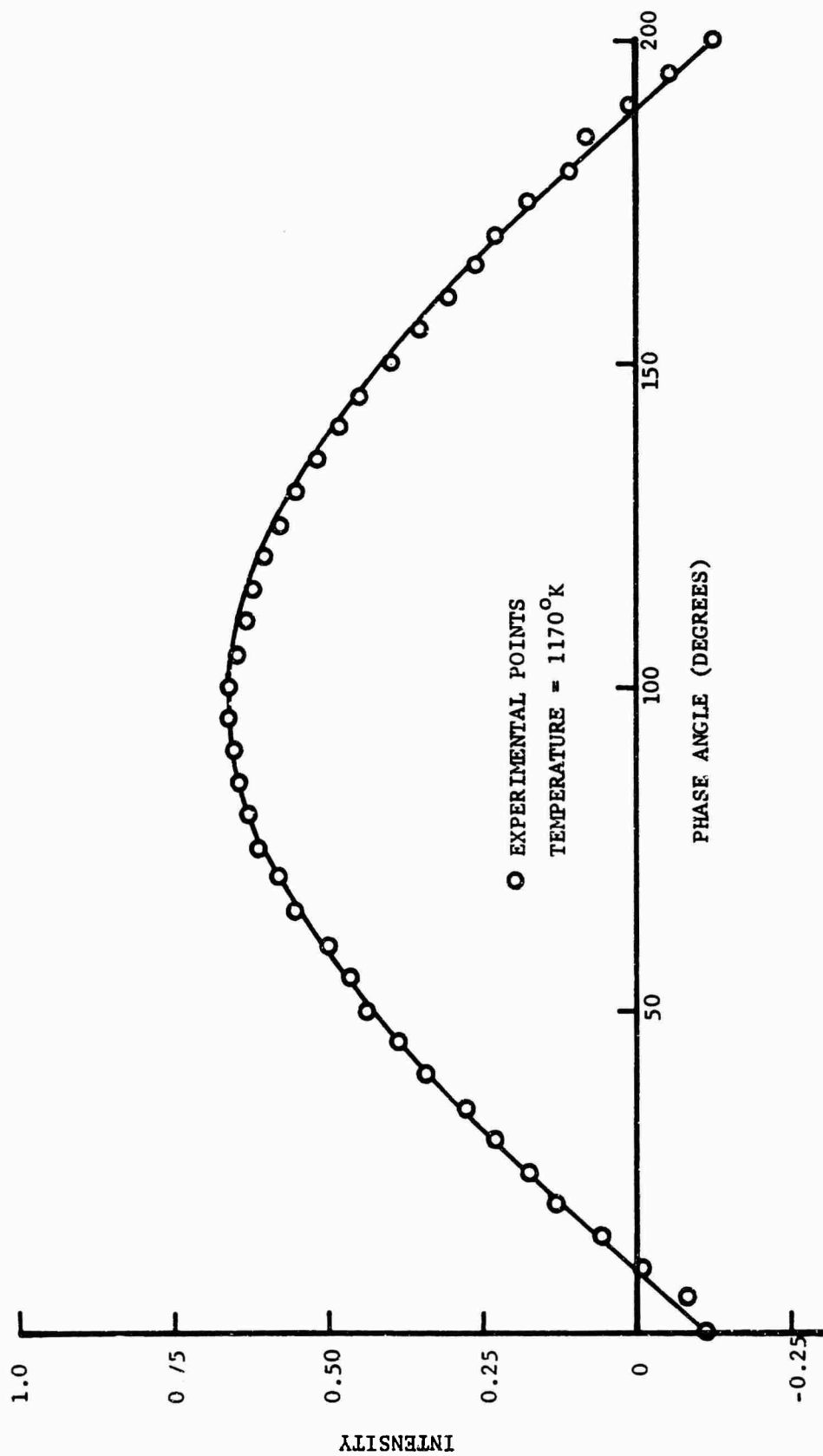


FIGURE 7. COMPARISON OF EXPERIMENTAL POINTS WITH THEORETICAL CURVE FOR SILVER

interpreted as an increasing contribution to the ions from fragmentation of higher polymers. It follows that increasing polymerization must occur at higher temperatures.

Deviation of the points given in Figure 5 from a smooth curve is a consequence of the precision of the experimental data. This was ± 0.5 degrees for the stronger ion signals and to ± 2 degrees for the weaker signals.

Referring to Table VI and Figure 5, again, a very real and perplexing observation is made that the phase angle obtained for LiF^+ is found to be smaller than the theoretical angle for LiF , particularly at temperatures below 1130°K. Such deviations require that LiF^+ be derived in part from some progenitor having a molecular weight less than LiF monomers.

The presence of such material is not very likely. An alternative explanation for the discrepancy may be due that certain conditions assumed in the theoretical treatment are not entirely satisfied. Among the possibilities are (1) departures from Maxwellian distribution of velocities in the gas, (2) non-molecular flow of gas through the orifice, (3) Li_3F_2^+ may not be a suitable reference, and (4) some unaccounted instrumental defect or distortion.

In order to cast some light on the importance of these effects, beam modulation experiments were carried on silver and lead, separately studied as standard materials to give data uncomplicated by fragmentation processes or by collision with co-vaporizing species. These metals were selected as reference materials because they are purported to vaporize only as monomers.

The experimental procedure used with these standard materials was as follows. Data on Pb^+ were taken at seven temperatures at 20-30° intervals between 912° and 1054°K, the temperature range in which the vapor pressure of silver is known to be small. After concluding the work on Pb, the temperature of the Knudsen cell was raised and the remaining Pb vaporized from the cell. Although complete removal of Pb was not achievable due to formation of Pb-Ag alloy, its ion intensity could be reduced to a value small enough as not to interfere with the subsequent Ag measurements. Data on Ag^+ were then acquired at 1170°, 1194° and 1223°K.

When the instrumental phase shift based on the theoretical and experimental phase angles for lead was applied to the experimental data for Ag^+ , the phase angles so obtained were found to be in good agreement with the theoretical values. This observation gives support to the validity of the theoretical treatment.

From the apparent normal behavior of these metals, it was suggested that they be used as internal standards to determine the instrumental phase zero correction in studies on the LiF system. This should provide a more absolute definition of the phase angles for the LiF species than is possible using Li_3F_2^+ as reference. Although either Ag or Pb would be suitable, lead rather than silver was chosen because it simplified the experiment. For example, after making the phase angle measurements on Pb^+ there was no need to completely vaporize the remaining lead before taking data on LiF species. Instead, it was found that elimination of lead vapor from the beam could be accomplished simply by raising the temperature of the Knudsen cell above the melting point of LiF and allowing the denser metal to sink below the surface of liquid LiF. Encapsulation was complete since no Pb^+ signal was subsequently detectable above or below the melting point of LiF.

In studies using lead as an internal reference, phase angles were determined on Pb and LiF in the order discussed above. Measurements on Pb were made at twelve temperatures, approximately 15° apart from 844° to 1000°K . Observations on the LiF system were taken over a wide range of temperatures (pressures) to determine the dependence of the phase angle on pressure.

Based on the Pb reference an average of $58.1^\circ \pm 1.3^\circ$ was obtained as the instrumental phase shift. This correction was applied to the LiF data and the results are presented in Table VII (values in parentheses). Values based on Li_3F_2^+ as reference are also given in the table (not in parentheses) and also graphically represented in Figure 8.

It is seen that the experimental phase angles for Li^+ and LiF^+ using the Pb reference are much smaller than the theoretical angles for LiF, angles determined for Li_2F^+ and Li_3F_2^+ are respectively found to be considerably smaller than those computed for Li_2F_2 and Li_3F_3 . The differences are observed to increase with temperature; Li_2F^+ and Li_3F_2^+ have larger temperature coefficients than Li^+ and LiF^+ . The close similarity in the temperature coefficient of the phase angle for Li^+ and LiF^+ species suggests that they are derived primarily from the same progenitor.

Use of Li_3F_2^+ as a reference species provides experimental phase angles for Li_2F^+ which are closely aligned with the theoretical value for Li_2F_2 . This indicates that the major proportion of Li_2F^+ is derived from Li_2F_2 . The angles for LiF^+ and Li^+ are, in this case, smaller than the theoretical value of LiF only below 1130°K ; above this temperature the observed angles become larger than theoretical. The most serious anomaly shown by this work, however, is the large difference in phase angle which is obtained using Pb as a reference species as compared to Li_3F_3 . This difference gets to be as large as 38 degrees at the higher temperatures. Neither this nor the other effects noted above can be explained by the beam modulation theory as presently formulated.

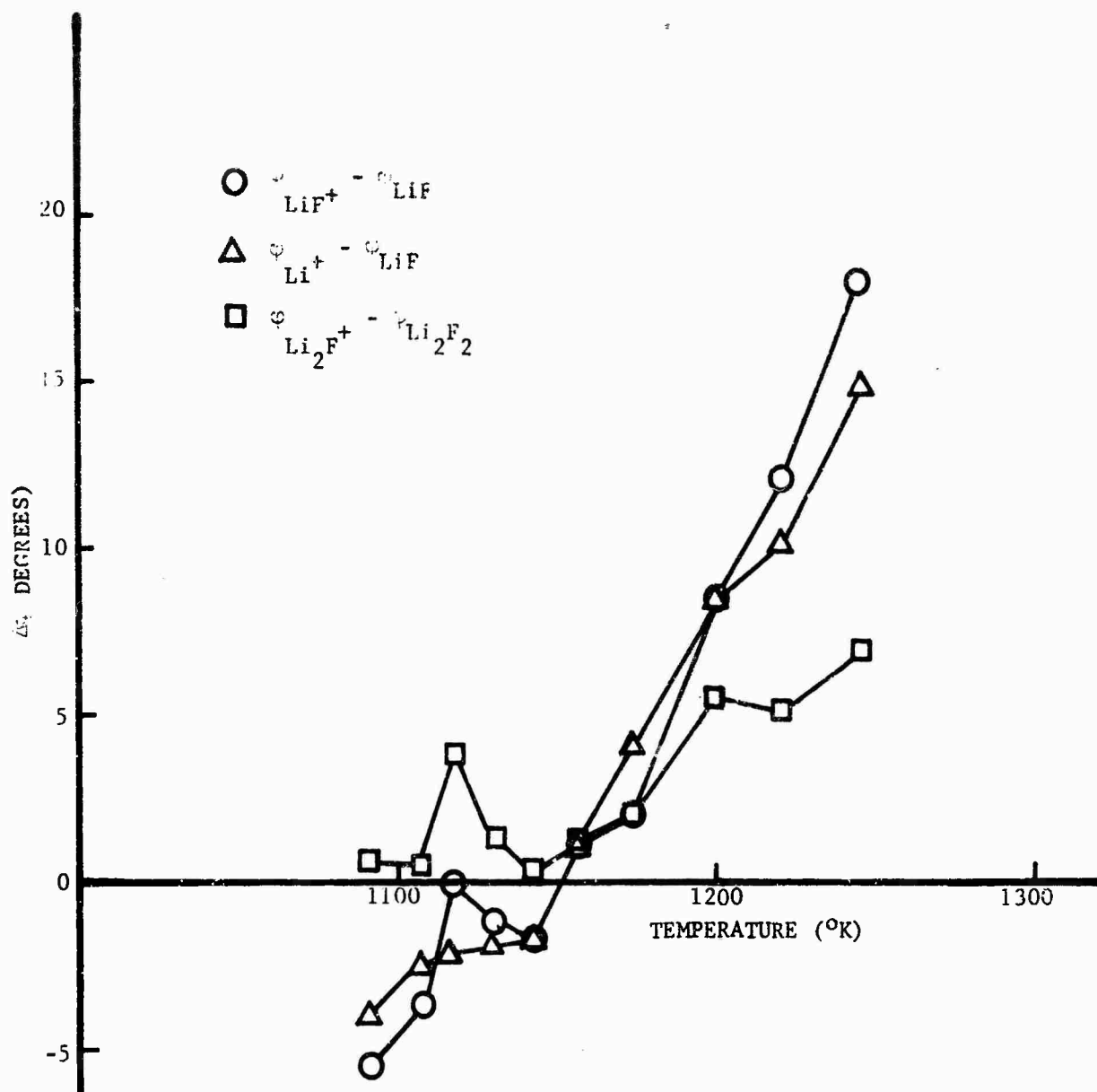


FIGURE 8. PLOT OF DIFFERENCE BETWEEN THE MEASURED PHASE ANGLES AND THE THEORETICAL PHASE ANGLES FOR THE MOST OBVIOUS PRECURSOR (REFERENCE: $\text{Li}_3\text{F}_2^+ - \text{Li}_3\text{F}_3$) VERSUS TEMPERATURE

TABLE VII

EXPERIMENTAL AND THEORETICAL PHASE ANGLES OF LiF SYSTEM AND LEAD

Precursor (Theoretical)	Ion (Experimental)	φ							
		1022°K	1044°K	1066°K	1079°K	1092°K	1108°K	1118°K	
LiF	Li ⁺	139.5	139	138.6	138.5	138.3	138	137.7	
		---	---	---	---	134.3	135.5	135.6	
		(123.1)	(125.1)	(125.1)	(122.1)	(123.1)	(122.1)	(120.1)	
Li ₂ F ₂	LiF ⁺	---	---	---	---	132.8	134.5	137.6	
		---	---	(123.1)	(124.1)	(121.6)	(121.1)	(122.1)	
	Li ₂ F ₂ ⁺	164	163	162.3	162	161.6	161	160.7	
		---	---	---	---	163.3	161.5	164.6	
		(154.1)	(153.1)	(151.1)	(151.1)	(152.1)	(148.1)	(149.1)	
Li ₃ F ₃	Li ₃ F ₂ ⁺	181.2	180	179	178.7	178.3	177.5	177.1	
		---	---	---	---	178.3	177.5	177.1	
						(167.1)	(164.1)	(161.6)	

TABLE VII (Contd.)

Precursor (Theoretical)	Ion (Experimental)	φ						
		<u>1131°K</u>	<u>1143°K</u>	<u>1157°K</u>	<u>1174°K</u>	<u>1202°K</u>	<u>1221°K</u>	<u>1246°K</u>
LiF	Li ⁺	137.4	136.7	136.4	135.9	135	134.4	133.5
		137.7	134.9	137.5	140	143.5	144.5	148.4
		(122.1)	(119.1)	(120.1)	(119.1)	(117.1)	(110.1)	(109.1)
Li ₂ F ₂	LiF ⁺	136.2	134.9	137.5	138	143.5	146.5	151.4
		(120.6)	(119.1)	(120.1)	(117.1)	(117.1)	(112.1)	(112.1)
		160.4	159.7	159.4	158.9	158	157.4	156.5
Li ₃ F ₃	Li ₂ F ⁺	161.7	160	160.5	161	163.5	162.5	163.5
		(146.1)	(145.1)	(143.1)	(140.1)	(137.1)	(128.1)	(124.1)
		176.7	175.9	175.5	174.8	174	173.0	171.9
Li ₃ F ₃	Li ₃ F ₂ ⁺	176.7	175.9	175.5	174.8	174	173.0	171.9
		(161.1)	(159.1)	(158.1)	(154.1)	(147.6)	(138.5)	(132.6)

Ionizing electron energy = 70 e.v.

Phase angles given in parentheses were obtained by using an instrumental phase zero correction of $58.1^{\circ} \pm 1.3^{\circ}$ as determined from 12 data points on lead reference over the temperature range $844^{\circ} - 1000^{\circ}\text{K}$.

Although a suitable interpretation of the phenomena of certain ions appearing at phase angles smaller than the theoretical value based upon their lightest possible precursors was not established, it is strongly suspected that a major part of the problem resides in departure from a Maxwellian distribution of velocities in the gas. Wahlbeck and Wang¹⁶ have reported that for a molecular beam emanating from a non-ideal right-circular cylindrical effusion orifice with a length-to-diameter ratio of 0.467 the velocity distribution shows deviations from Maxwellian in the direction of an excess of high speed molecules. The deviation increased (1) with increasing orifice length, and (2) with decreasing Knudsen number (ratio of mean free path in the effusion cell to orifice diameter) in the transition region.

In our experiments discussed above, a conical orifice with a channel length to diameter ratio of approximately 0.3 was used. This is sufficiently close to the Wahlbeck and Wang orifice of $L/D = 0.467$ to suggest that in our case also the velocity distribution departed from Maxwellian. Therefore, work on the LiF system was repeated using a tungsten cell fitted with a stainless steel lid having a near-ideal orifice (orifice length-to-diameter ratio of 0.04). In these experiments metallic sodium was placed in the cell along with LiF and Pb so that data on sodium could also be taken. The experiment involved phase angle measurements on Na^+ over the temperature range from 483° to 565°K . After concluding the work on sodium, the temperature of the cell was raised and the remaining sodium vaporized. Data on Pb^+ were then acquired. Following this and prior to taking the data on LiF species, the Pb vapor was eliminated from the molecular beam by raising the temperature of the cell above the melting point of LiF and allowing the denser metal to sink below the surface of the molten LiF. By this technique data uncomplicated by lead vapors were obtained on LiF. Sodium was chosen because (1) its molecular weight is nearly the same as that for LiF, and (2) its vapor is almost entirely monomeric below 600°K . Pb was used as a reference material to fix the instrumental phase shift.

The phase angles for LiF were determined at three temperatures. The results corrected to Pb reference were in good agreement with earlier data. Thus, the change in the orifice parameters seemed to have no apparent effect on the phase angles. When the Na^+ data were appropriately corrected for the instrumental phase shift the phase angles were on the average $17.4^\circ \pm 1.4^\circ$ smaller than the theoretical values.

As a final experiment, a change in the design of the chopper wheel was made. The change was based upon the concept that the slots in the wheel have the nature of orifices and will have an effect on the velocity distribution analogous to that of the orifice in the cell. The orifice characteristics of the chopper wheel will be expected to depend not only on the thickness-to-width ratio, but also on the wheel speed. The wheel was accordingly redesigned to be thinner, and the trailing and leading edges of each sector were machined to give sharp edges, beveled at 30° to the wheel surface.

Time and funds permitted measurements on sodium and lead only with the new wheel. Using the Pb reference to fix the instrumental phase zero position, the experimental phase angles for Na^+ were found to be 11° smaller than the theoretical values, a significant improvement over the 17° observed earlier. This result suggests the importance of the chopper design, its significance, however, cannot be fully realized until further work is conducted in which other wheel designs and other vapor species are tested.

A second possible source of the discrepancy between theoretical and experimental phase angles resides in the band width of the signal channel amplifier. Since the information regarding the velocity distribution in the molecular beam is defined by the shape of the wave produced by a train of ion pulses it is essential that this wave be undistorted. Tests carried out previously² to determine the fidelity of the amplifier have shown that the signal was slightly distorted; the extent of this distortion was considered, however, to be within acceptable limits. We now feel, after gaining a better understanding of the beam modulation method that a wider band amplifier capable of producing a distortion free signal is needed.

Although a satisfactory explanation for the anomaly in the LiF results has not been obtained to date, it is believed very strongly that the explanation resides in a combination of factors such as those discussed above. Their further exploration and clarification should result in the development of beam modulation as a very powerful adjunct to high temperature mass spectrometry.

4.3.1 D.C. ION INTENSITY MEASUREMENT OF SATURATED LiF VAPOR

After the initial work on the beam modulation experiments, d.c. ion intensities were measured over the temperature range from 1119 to 1180°K for the four ion species of interest. The second-law heat from the slope of $\log I^+T$ versus $1/T$ was found to be approximately 15-20 kcal too low, although Ag data taken under similar conditions gave satisfactory heats. It is recalled from earlier torsion effusion work carried out in this laboratory to determine the vapor pressure of LiF over the liquid phase that difficulties associated with creeping of the sample through the orifice were encountered.¹⁷ No evidence of such behavior has been observed in our mass spectrometric studies. The problem may be a consequence of the long "drift space" used, resulting in collisions in the beam. Such collisions could alter the gas temperature and give rise to abnormal second-law heats. If this is the case, the problem can be eliminated by the removal of the "drift space."

4.4 STUDIES ON THE LiCl SYSTEM

Due to lack of time only preliminary data were obtained on this system. Lithium chloride crystals and sodium metal were placed in a beryllia cell liner fitted with a stainless steel lid having a near-ideal orifice (orifice length-to-diameter ratio of 0.04) and heated. Phase angle measurements of the vapor species so obtained were taken in the manner already discussed using the "thick" chopper wheel. The phase positions of the pure precursors and the phase angles of the ion species based on the sodium reference are given in Table VIII. Lead could not be used as reference because its vapor pressure would complicate the LiCl data at the temperatures of the experiment.

TABLE VIII
EXPERIMENTAL AND THEORETICAL PHASE ANGLES
OF LiCl SYSTEM AND SODIUM

Precursor (Theoretical)	Ion (Experimental)	ϕ			
		869°K	892°K	925°K	933°K
LiCl		160	159.4	158.2	158
	Li ⁺	177.4	173.4	168.4	169.4
	LiCl ⁺	---	165.4	158.4	156.4
Li ₂ Cl ₂		190	189	187.2	187
	Li ₂ Cl ⁺	200.4	198.4	195.4	188.4
Li ₃ Cl ₃		212	210.7	208.3	208
	Li ₃ Cl ₂ ⁺	---	---	---	206.4

Ionizing electron energy = 70 e.v.

Instrumental phase zero correction of $82.4^\circ \pm 2.4^\circ$ was obtained from four data points on sodium reference taken over the temperature range 525° to 594°K.

The data show that (1) Li⁺ has two precursors, LiCl and Li₂Cl₂, (2) LiCl⁺ is derived entirely from LiCl, and (3) the amount of Li₂Cl⁺ derived from Li₂Cl₂ and Li₃Cl₃ changes with temperature, the fraction coming from the dimer increases with increasing temperature. Although no glaring anomalies are apparent in these results, too much significance should not be attached to them until the discrepancy observed earlier between the Pb and Na references is reconciled.

SECTION 5

ENVIRONMENTAL SAMPLING DATA REPORT

5.1 INTRODUCTION

The Industrial Hygiene and Safety Program for Contract No. FO4611-68-C-0012 has been successfully completed. The Health and Safety efforts have met all work phases including final decontamination and disposal operations. No beryllium incidents occurred on the project.

5.2 DISCUSSION

a. General air sampling equipment used throughout the program was effective, however, some deterioration in the performance of motors and batteries was found after moderate, non-continuous usage. This phenomenon was evidenced primarily in the Staplex High Volume Samplers. The volumetric flowrate dropped from 18 cfm at the onset of this program to 11 cfm at its conclusion.

As an important adjunct of the sampling program, wipe samples were taken at random through the working area. Since this type of sampling is after the fact, only verification of cleanup and decontamination procedures is intended in reporting these figures. Indication of toxic particle generation during work processes would be evident in sample results if these procedures had not been thorough.

Relatively high wipe sample results were found on the transfer bench during initial operation, however, after the masonite bench top was refurbished with a formica top, particulate levels were reduced to well below acceptable limits.

The reliability of the exhaust pre-filter, absolute filter and exhaust system, verified by out-plant sample statistics, is presented later in this report.

Disposable waste was placed in sealed plastic bags which in turn were placed in sealed steel barrels. These barrels were picked up and properly disposed of by an approved disposal company.

Laundryable lab coats were changed daily during the program by all workers. A vendor qualified to launder potentially contaminated clothing of this type collected the sealed bags containing the soiled coats and delivered clean coats weekly.

Post program medical examinations are complete. There has been no evidence of pneumocomiosis in any of the workers and their records are closed out for the project.

b. Sample Collection. Samples were collected on Whatman 41 filter paper using standard high volume and low volume samples. No respirable attachment was used on these samples nor was particle size considered in the sampling technique. This conservative approach resulted in higher gross weight per sample collected. This is due to the collection of particulates greater than 10 microns. Flow rates for the high volume samples ranged between 18 and 11 cfm. Personnel monitor samples were collected at 4 to 5 liters per minute. Sample collection stations remained constant during the course of the program, with respect to processes and meteorological conditions.

c. Statistical Inference of Beryllium Samples. A total of 28 environmental samples were collected during the course of the program. The results appear in Tables IX, X, XI, XII, and XIII.

TABLE IX. AIR SAMPLING DATA

Filter No.	Date	Location	Operation	Sampler Type	Run Time (min)	Rate (cfm)	Results (μg)	Computed Exposure ($\mu\text{g}/\text{m}^3$)
1	10/20/67	Workbench	Transfer	Staplex Hi-Vol	120	18	< 0.02	< 0.0003
2	10/20/67	Mass Spectrometer	Run	Staplex Hi-Vol	120	18	< 0.02	0.0003
4	11/08/67	Mass Spectrometer	Run	Staplex Hi-Vol	240	11	< 0.40	0.0053
7	11/09/67	Operator	Transfer	MSA Monitaire	40	18	< 0.02	0.0035
8	11/09/67	Out Plant #1	Transfer and Run	Unico Hi-Vol	420	18	< 0.02	0.00009
9	11/09/67	Out Plant #2	Transfer and Run	Unico Hi-Vol	420	18	< 0.02	0.00009
10	11/10/67	Mass Spectrometer	Run	Staplex Hi-Vol	255	15	< 0.02	0.0002
18	12/04/67	Workbench	Transfer	Staplex Hi-Vol	300	11	< 3.1	0.033
19	12/04/67	Out Plant #1	Transfer	Unico Hi-Vol	300	18	< 0.02	0.00013
20	12/04/67	Out Plant #2	Transfer	Unico Hi-Vol	300	18	< 0.02	0.00013
21	12/04/67	Operator	Transfer	MSA Monitaire	20	14	< 0.02	0.009
22	12/04/67	Mass Spectrometer	Run	Staplex Hi-Vol	135	11	0.16	0.0038
24	01/16/68	Mass Spectrometer	Run	Staplex Hi-Vol	210	14	2.5	0.03
25	01/22/68	Mass Spectrometer	Transfer	Staplex Hi-Vol	360	14	4.3	0.03

TABLE X. WIPE SAMPLE DATA

Filter No.	Date	Location	Area ft ²	Operation	Lab Results (μ g)	Computed Exposure (μ g/ft ²)
3	11/8	Work Bench (Center)	1.0	Pre Transfer	0.52	0.52
5	11/8	Work Bench (Right)	1.0	Post Transfer	6.70	6.70
6	11/9	Sink	1.0	Post Cleanup	2.00	2.00
11	11/13	Work Bench (Center)	1.0	Post Transfer	0.46	0.46
12	11/16	Sink	1.0	Post Transfer	0.77	0.77
13	11/16	Work Bench (Center)	1.0	Post Transfer	1.7	1.7
14	11/16	Ladder Near Sink	1.0	Post Transfer	0.03	0.03
15	12/4	Work Bench (Right)	1.0	Post Transfer	0.70	0.70
16	12/4	Work Bench (Left)	1.0	Post Transfer	0.94	0.94
17	12/4	Work Bench (Center)	1.0	Post Transfer	5.70	5.70
23	12/5	Work Bench (Left)	1.0	Post Transfer	0.42	0.42
26	1/22	Sink	1.0	Post Cleanup	1.0	1.0
27	1/23	Work Bench (Left)	1.0	Post Cleanup	0.25	0.25
28	1/23	Work Bench (Right)	1.0	Post Cleanup	0.09	0.09

NOTE: Sampling Media - Whatman 41 Filter Paper

TABLE XI
TOTAL SAMPLE RESULT SUMMARY

<u>No. Samples Taken</u>	<u>Type and Location</u>	<u>Hours Sampled</u>	<u>Ave₃ μg/m³</u>	<u>Max₃ μg/m³</u>
2	Personnel MSA Transfer Area	1	0.0062	0.009
8	High Volume Transfer Area	29	0.013	0.033
4	High Volume Out Plant	24	0.0001	0.00013
14	Wipe Samples	N/A	1.25 μg/ft ²	6.70 μg/ft ²

TABLE XII

DESCRIPTIVE STATISTICS FOR 14 BERYLLIUM AIR SAMPLE RESULTS

<u>Description</u>	<u>$\mu\text{g}/\text{m}^3$</u>
Range:	0.03291
Mode:	Trimodal 0.003, 0.00009, 0.03
Mean:	0.00828
Median:	0.00185
Standard Deviation:	0.012
Coefficient of Variation:	1.58

NOTE: T. L. V. = $2 \mu\text{g}/\text{m}^3$

TABLE XIII

DESCRIPTIVE STATISTICS FOR 14 BERYLLIUM WIPE SAMPLE RESULTS

<u>Description</u>	<u>$\mu\text{g}/\text{ft}^2$</u>
Range:	6.67
Mode:	Non-Existent
Mean:	1.52
Median:	0.73
Standard Deviation:	1.91
Coefficient of Variation	1.25

The mean value as indicated in Table XII is less than one half of 1% of the acceptable threshold limit values (T. L. V.) for beryllium in air exposure. The median and mode are substantially less than the reported mean, thereby indicating a large number of random samples occurring near the lower limit of the distribution. This was due in part to the lower limit of sensitivity of the reporting laboratory instrumentation, which was 2×10^{-2} micrograms total weight. Upon receipt of results indicating "less than 2×10^{-2} micrograms," the assumption was made to regard the results as an absolute value of 2×10^{-2} micrograms. This conservative approach increased the mean value and adjusted the distribution nearer the upper limit.

5.3 SUMMARY AND CONCLUSIONS

- (1) All objectives of the Industrial Hygiene and Safety Program Plan were met during the course of the program.
- (2) No exposures to beryllium exceeded the Threshold Limit Values.
- (3) All biomedical examinations were negative for pneumoconiosis.

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16. ABSTRACT		
<p>This document is the final report on Contract FO4611-68-C-0012. Mass spectrometric studies of various vapor species produced in the H_2-BeO and in the $HCl-BeO$ systems under Knudsen conditions were carried out at temperatures up to $2485^\circ K$. Appropriate equilibrium reactions involving these species were used to determine the heat of formation of $BeOH(g)$. A weighted average of -22.5 kcal/mole is indicated for $[Hf_{298}^{0}-BeOH(g)]$, and the uncertainty is estimated to be ± 6 kcal/mole. (U)</p> <p>Examination of the mass spectrum for vapor species having the composition $(BeO)_n-H_2O$, where $n = 1$ through 5, was conducted. Detectable quantities of such species were not found to be present in the H_2-BeO system. (U)</p> <p>Reaction of graphite and beryllium oxide was studied by means of the torsion effusion techniques. Steady-state torsion pressures were not obtainable. (U)</p> <p>The remaining effort was directed to the redetermination of the fragmentation pattern of the vapor species in the LiF system. A mass spectrometric technique involving beam modulation and phase sensitive detection was used. (U)</p>		

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Molecular beam modulation
Phase sensitive detection
 LiI(g)
 LiCl(g)
Taporization of BeO
 BeOH(g)

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